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Comparison between Zeeman and Continuum Background Correction for Graphite Furnace AAS on Environmental Samples

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COMPARISON BETWEEN ZEEMAN AND CONTINUUM BACKGROUND CORRECTION FOR GRAPHITE FURNACE AAS ON ENVIRONMENTAL SAMPLES*

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ABSTRACT

A comparison study was carried out to evaluate the two most commonly used background correction techniques in furnace atomic absorption spectroscopy, Zeeman effect and continuum source background correction. Synthetic sample matrices were prepared consisting of the most frequently determined furnace elements in environmental waste samples. Arsenic, selenium, thallium, lead, and antimony were determined in high concentration matrices of aluminum, iron, sodium, potassium, calcium, magnesium, titanium, and phosphorus by furnace atomic absorption spectroscopy using the Zeeman and continuum lamp background correction techniques. The results of this study showed that with identical instrumentation, the Zeeman effect background correction technique provided interference-free analysis in most cases where the continuum source background correction technique failed to correct structured backgrounds.

INTRODUCTION

Environmental Protection Agency (EPA) programs require the development and testing of appropriate methods for the determination of environmentally important trace metals in hazardous waste samples. Graphite furnace atomic absorption spectroscopy (AAS) is well-established as the method of choice for most of these trace metals (1,2). Table I compares the Superfund contract required detection limits (CRDL), required by the EPA, with the detection limits available by the Zeeman corrected graphite furnace AAS (3). The Zeeman furnace data have been calculated by assuming that characteristic mass data are within ± two times the detection limit and that the sample volume is 20 μL. Of the 19 elements listed, all have much better detection limits than the CRDL required by the EPA. Selenium has the poorest ratio of available to required detection limits (about 3-fold). Except for selenium, all of the test elements have better than 10-fold ratios of available to required detection limits.

However, considerable concern is expressed in the literature for interferences when these trace metals are determined by graphite furnace in environmental sample matrices. The interferences often result from deficiencies in the continuum source background correction systems used in many furnace instruments. The Zeeman background correction is reported to be able to remove many of these errors. This study was undertaken to make a direct comparison of the continuum source and Zeeman background correction techniques for the determination of five important elements (As, Se Tl, Sb, and Pb) in eight matrices (K, Na, Ca, P, Mg, Ti, Al, and Fe).

To assure the validity of the comparison, the same instrument model was used with the two different background correctors. In all cases, identical stabilized temperature platform furnace (STPF) methods were used in both instruments. The methods were very similar to those used by Manning and Slavin (4) who used continuum background correction with STPF procedures.

TABLE I
Elements Determined by Graphite Furnace Atomic Absorption Spectroscopy

Element	*Required detection limit (μg/L)*	*Detection limit Zeeman AAS (μg/L)*
Aluminum	200	0.5
Antimony	80	2.0
Arsenic	10	1.0
Barium	200	0.4
Beryllium	5	0.05
Cadmium	5	0.02
Chromium	10	0.15
Cobalt	50	0.35
Copper	25	0.4
Iron	100	0.25
Lead	5	0.5
Manganese	15	0.1
Nickel	40	0.5
Selenium	5	1.5
Silver	10	0.07
Thallium	10	1.0
Tin	40	1.2
Vanadium	50	2.0
Zinc	20	0.02

EXPERIMENTAL

Two Perkin Elmer® Model 5000 atomic absorption spectrometers were used: one equipped with both a deuterium lamp and a tungsten lamp background correction system;

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the other equipped with a Zeeman background correction system. The HGA-500 furnace, AS-50 autosampler, and DS-10 Data Station were used on both instruments. As recommended by Perkin-Elmer (6), pyrolytically coated graphite tubes were used with a L'vov platform. Electrodeless discharge lamps were used for all of the test analytes. The operating conditions are shown in Figure 1 and listed in Table II. The times used for the furnace analyses steps are shown in Figure 1. Argon purge gas flow remained at 300 mL/min, except during the atomization step when it was stopped. The integration time was 6 seconds in all cases; although only a 4-second time interval of those data is shown in the subsequent figures. The recently recommended cool-down procedure (7) was used.

In most cases, the concentration of test solutions was chosen to provide an integrated absorbance, A•s, between 0.1 and 0.3 A•s. In all cases, the test samples, with or without potential interferents, were delivered in 20-μL aliquots followed by 5-μL aliquots of the matrix modifier shown in Table II. Appropriate blanks were measured for the matrix materials and the potential interferents. All blank, standard, and test solutions were prepared in 0.5% HNO_3. All of the matrix interferent elements, except for the Al interference on As and the Fe interference on Se, were at a concentration of 500 or 1000 mg/L. For the As test, the Al concentration was 50 mg/L because the interference produced by Al was very large. For Se, the Fe concentration used was 100 mg/L. The solutions used to study interferences were prepared from 1000 mg/L standards obtained in 1% HNO_3 (Spex Industries, Inc., Edison, NJ). In the case of Al and Fe, these solutions were diluted to 100 mg/L in 1% HNO_3. The P solution was made up from H_3PO_4.

While both peak absorbance and integrated absorbance (A•s) signals were recorded, only the integrated signals have been reported in this paper. Potential interferents often changed the peak shape. This change usually affected the peak absorbance but had little or no effect upon the integrated absorbance signal, A•s. In all cases, standardization was made against aqueous solutions containing only the analyte of interest and the matrix modifier.

The characteristic mass, defined as the quantity of analyte (expressed as μg) that produces an integrated absorption peak area of 0.0044 A•s (5), provides an indication of instrument sensitivity and performance (3).

RESULTS

The experimental procedure consisted of testing the effect of eight matrices on five analytes using the two background correction systems. In most of the resulting 40 experiments, both background correction systems provided acceptable results. Those situations where a problem was found are discussed in the following text.

Arsenic

Aluminum and phosphorus interfered very strongly in the determination of As with the continuum background-corrected system. The interference of Al on As is well-documented (8,9). Aluminum causes a positive error with 50 mg/L Al producing an apparent As signal larger than 50 μg/L (Figure 2). The interference is eliminated when Zeeman background correction is used. In this and the rest of the comparison figures, the amount of material is shown below the absorbance profiles that produced those profiles, 50 μg/L As for the upper pair of Figure 2. For the middle pair, the profile was produced by 500 mg/L of P (as H_3PO_4). The lower pair of profiles was produced by the mixture of As and P solutions.

Phosphorus has a negative effect on As analysis, as shown in Figure 3, when using continuum background correction.

TABLE II
Operating Conditions

Temperature (°C)	*As*	*Se*	*Tl*	*Sb*	*Pb*
Dry	160	160	160	160	160
Char	1100	1100	600	1200	900
Atomize	2500	2500	1400	2400	1900
Cool	20	20	20	20	20
Wavelength (nm)	193.7	196.0	276.8	217.6	283.3
Matrix modifier	1% $Ni(NO_3)_2$	1% $Ni(NO_3)_2$	H_2SO_4	$Ni(NO_3)_2$ + 0.025% $Mg(NO_3)_2$	$NH_4H_2PO_4$ + 0.07% $Mg(NO_3)_2$

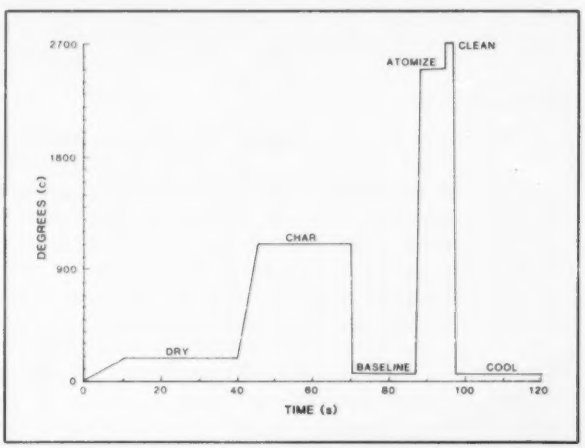

Fig. 1. Temperature program for the furnace.

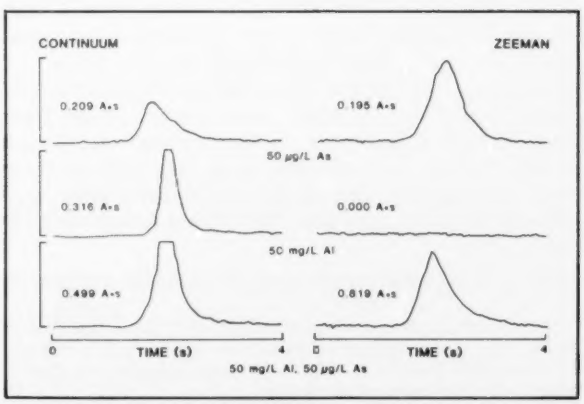

Fig. 2. Absorbance profiles for 50 μg/L of As (1 ng) in 50 mg/L of Al.

This interference, caused by structured background, has been documented by many workers (10,11). The structured background did not produce a negative signal with Zeeman background correction. Nevertheless, only a 50% recovery of As in the presence of 500 mg/L P was obtained using Zeeman background correction. Possibly the 1100 °C char temperature may have been too high for As in the presence of phosphorus. The measurements were repeated using a char temperature of 800 °C, and the effect of increasing concentrations of P on the recovery as As is shown in Figure 4. The results indicate that as P increases in the matrix, the As percent recovery decreases, which is in conflict with the finding of Fernandez and Giddings (11). They observed that 500 mg/L P (as calcium phosphate) provided the expected negative error using continuum background correction but had no effect on As using Zeeman background correction. The source of phosphorus may explain the different observations in this work and in that of Fernandez and Giddings. This discrepancy merits further investigation.

Selenium

Both P and Fe interfered with the determination of Se when continuum background correction was used, agreeing with results reported in the literature (10,11). Phosphorus (1000 mg/L) produces a large negative signal with an integrated absorbance which swamps the integrated absorbance from 50 μg/L Se, as seen in Figure 5. From the figure, peak height would be a better means of quantification if using continuum background correction. The negative signal was not present with Zeeman background correction. Phosphorus exhibited no significant effect on Se when using the Zeeman background correction, which is in agreement with previously reported data (12).

The interference of Fe on Se determination when using continuum background correction is well known (13). This interference is shown in Figure 6. No interference of Fe on Se was observed when using the Zeeman background correction system (Figure 6).

In Figure 7 it is seen that 500 mg/L of Ti had an effect upon the Se signal with the continuum background correction system. But K, Na, Ca, Mg, and Al did not affect the Se signal using continuum correction.

Thallium

For thallium determination, both Na and K presented some analytical difficulty with both background correction systems. The effect of 1000 mg/L K is shown in Figure 8 and of 1000 mg/L Na in Figure 9. The magnitude of the interference for both matrices and both background correction systems

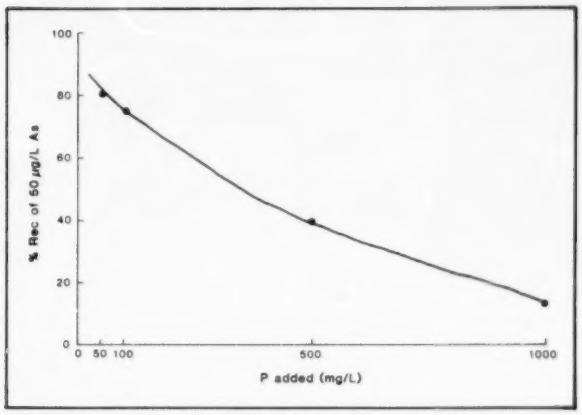

Fig. 4. The effect of P (as H_3PO_4) on the recovery of arsenic (Zeeman background correction).

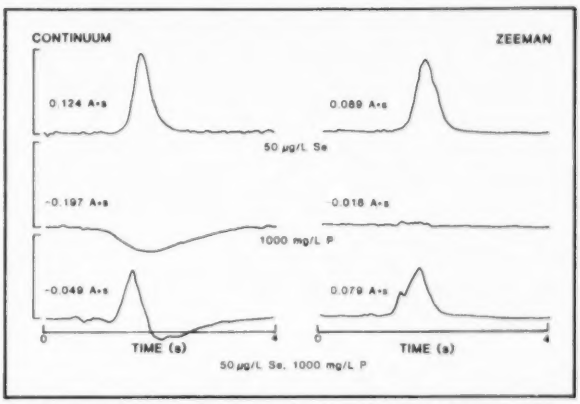

Fig. 5. Absorbance profiles for 50 μg/L of Se in 1000 mg/L of P.

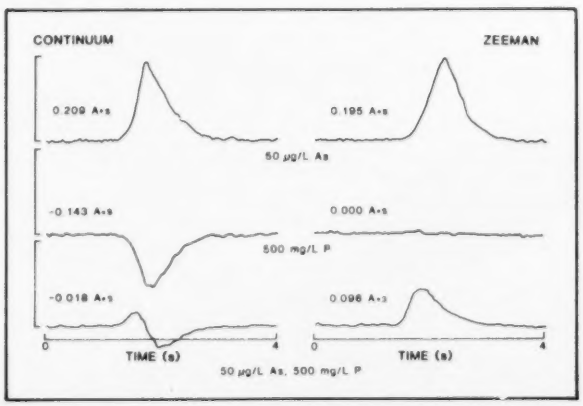

Fig. 3. Absorbance profiles for 50 μg/L of As in 500 mg/L of P, as H_3PO_4.

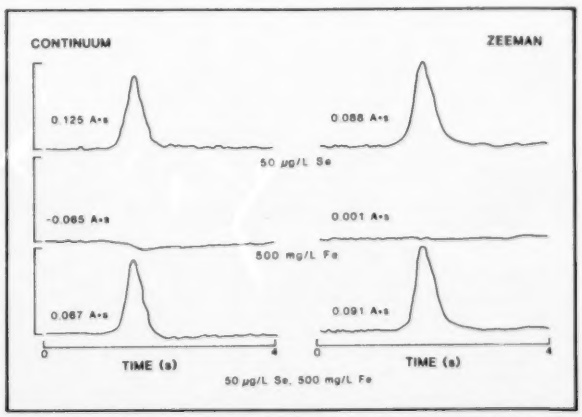

Fig. 6. Absorbance profiles for 50 μg/L of Se in 500 mg/L of Fe.

is similar, indicating that the effect may not be related to differences in the background correction system. A possible explanation is analyte loss during the char cycle due to an inadequate matrix modifier. Recent information suggests that sulfuric acid is not an optimum matrix modifier and that palladium may be preferable for this application (14).

Antimony

The effect of Fe on Sb determination is shown in Figure 10. Iron interferes in the determination of Sb when the continuum background correction system is used (11). There was no interference from Fe when Zeeman background correction was used.

Figure 11 shows the effect of Al on Sb, indicating a typical over-correction error with the continuum background correction system, if the peak height mode were used. However, the literature does not report such an interference (15) and a search of the wavelength tables does not indicate that Al has any strong line close to the 217.6-nm line of Sb.

Lead

Figure 12 shows the influence of Fe on the Pb determination. This was not expected. Some signal suppression was experienced with both correction systems. More detailed work is planned using various matrix modifiers to improve analytical efficiency for Pb.

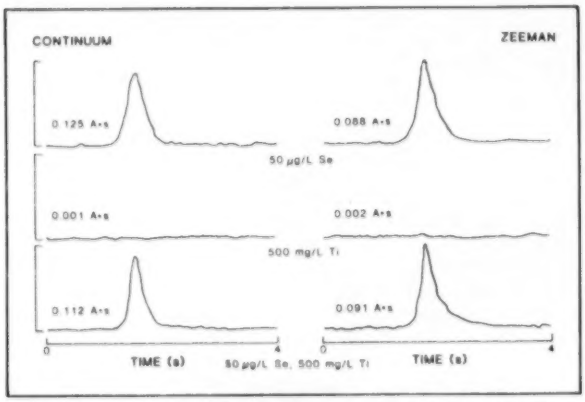

Fig. 7. Absorbance profiles for 50 µg/L of Se in 500 mg/L of Ti.

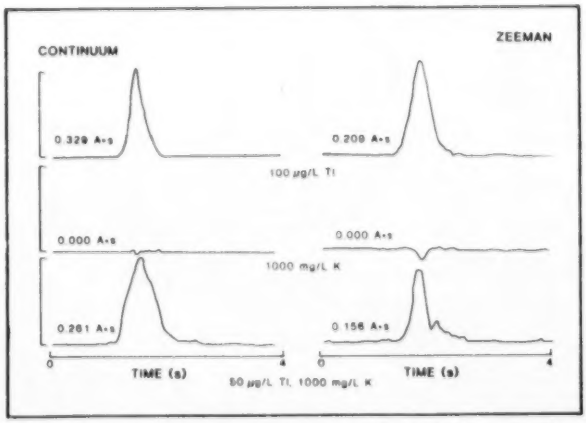

Fig. 8. Absorbance profiles for 100 µg/L of Tl in 1000 mg/L of K.

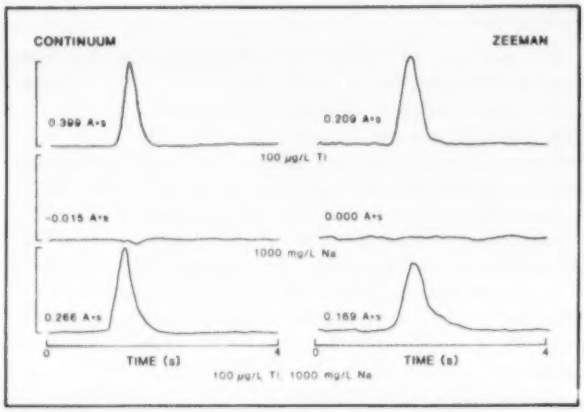

Fig. 9. Absorbance profiles for 100 µg/L of Tl in 1000 mg/L of Na.

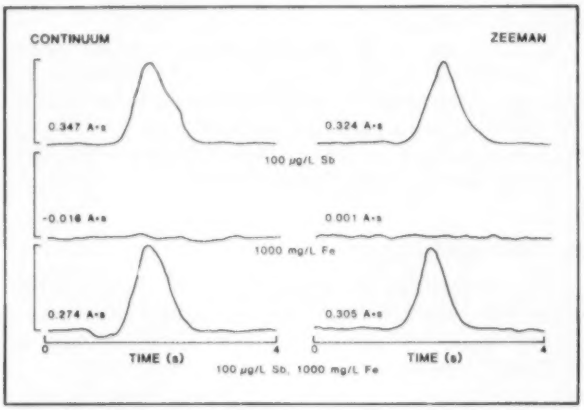

Fig. 10. Absorbance profiles for 100 µg/L of Sb in 1000 mg/L of Fe.

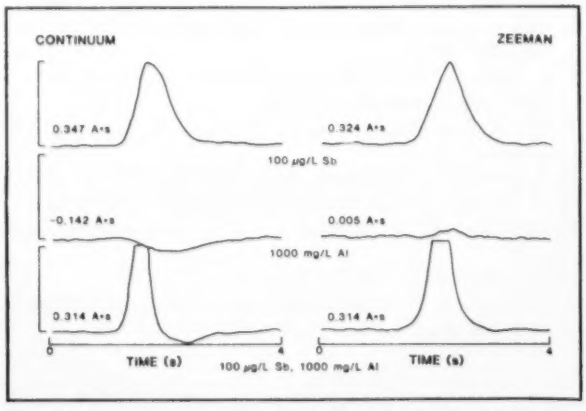

Fig. 11. Absorbance profiles for 100 µg/L of Sb in 1000 mg/L of Al.

SUMMARY

Five elements in eight potentially interfering matrices were studied using the Zeeman effect and continuum lamp background correction systems on two Perkin Elmer Model 5000 AAS instruments. Agreement among the results was very good. Simple aqueous standards were used containing only the matrix modifier in addition to the analyte. The interference results that were found with continuum background correction are given in Table III. Interferences were observed from P and Al on As determination; from P and Fe on Se determination; from K, Na, Ca, Ti, and Fe on Tl determination; from Fe, Al, and Ti on Sb determination; and from Fe on Pb determination. The equivalent chart for Zeeman background correction is given in Table IV.

Interferences were observed from Na, K, and Ca on Tl determination and from P on As determination. The Tl interferences may be the result of a matrix modifier deficiency rather than a Zeeman background correction problem, since similar interferences were observed with continuum background correction. The P interference on As determination conflicts with reports in the literature (11). Apparently, P interference may be related to the form of P added [e.g., H_3PO_4 or $Ca_2(PO_4)_3$].

In conclusion, the use of the Zeeman background system significantly reduces background interferences from common matrix elements for the determination of As, Pb, Sb, Se, and Tl. Its use is preferred over continuum background correction systems for the analyses of environmental samples with widely varying sample matrices.

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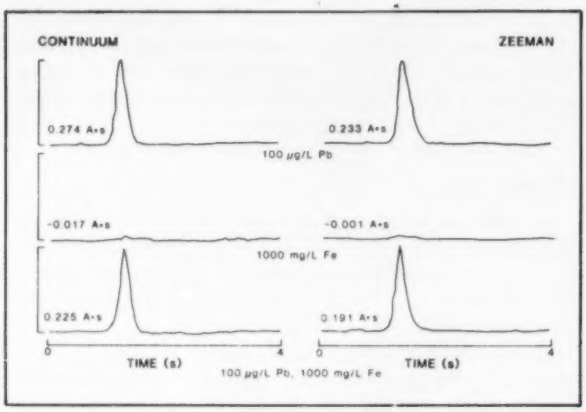

Fig. 12. Absorbance profiles for 100 µg/L of Pb in 1000 mg/L of Fe.

TABLE III
Interferences, Continuum Background Correction

	Analyte				
Interferent[a]	*As*	*Se*	*Tl*	*Sb*	*Pb*
K	0	0	XX	0	0
Na	0	0	X	0	0
Ca	0	0	X	0	0
P	XX	XX	0	0	0
Mg	0	0	0	0	0
Ti	0	X	X	X	0
Al	XX	0	0	XX	0
Fe	0	XX	XX	XX	X

[a]1000 mg/L of each interferent, except 50 mg/L of Al and 100 mg/L of Fe.
0 = no interferences.
X = 5 to 20% interference.
XX = strong interference, over 20%.

TABLE IV
Interferences, Zeeman Background Correction

	Analyte				
Interferent[a]	*As*	*Se*	*Tl*	*Sb*	*Pb*
K	0	0	X	0	0
Na	0	0	X	0	0
Ca	0	0	X	0	0
P	X	0	0	0	0
Mg	0	0	0	0	0
Ti	0	0	0	0	0
Al	0	0	0	0	0
Fe	0	0	0	0	0

[a]1000 mg/L of each interferent, except 100 mg/L of Al and Fe.
0 = no interference.
X = 5 to 20% interference.

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